

I CLAIM:

1       1. A tubing/casing annulus plug additive comprising a  
2       dry mixture of a water soluble crosslinkable polymer,  
3       a crosslinking agent, and a reinforcing material selected  
4       from among fibers and comminuted plant materials.

1       2. The additive of claim 1 wherein the polymer is an a  
2       carboxylate-containing polymer and the crosslinking agent  
3       is a chromic carboxylate complex.

1       3. The additive of claim 2 wherein the reinforcing  
2       material comprises hydrophilic and hydrophobic fibers.

1       4. The additive of claim 3 wherein the hydrophobic  
2       fibers comprise at least one selected from the group of  
3       hydrophobic fibers consisting essentially of nylon,  
4       rayon, and hydrocarbon fibers, and wherein the  
5       hydrophilic fibers comprise at least one selected from  
6       the group of hydrophilic fibers consisting essentially of  
7       glass, cellulose, carbon, silicon, graphite, calcined  
8       petroleum coke, and cotton fibers.

1       5. The additive of claim 2 wherein the reinforcing  
2       material comprises comminuted plant material.

1       6. The additive of claim 5 wherein the reinforcing  
2       material comprises at least one comminuted material  
3       selected from the group of comminuted plant materials  
4       consisting essentially of nut and seed shells or hulls of  
5       almond, brazil, cocoa bean, coconut, cotton, flax, grass,  
6       linseed, maize, millet, oat, peach, peanut, rice, rye,  
7       soybean, sunflower, walnut, and wheat; rice tips; rice  
8       straw; rice bran; crude pectate pulp; peat moss fibers;  
9       flax; cotton; cotton linters; wool; sugar cane; paper;  
10      bagasse; bamboo; corn stalks; sawdust; wood; bark; straw;  
11      cork; dehydrated vegetable matter; whole ground corn  
12      cobs; corn cob light density pith core; corn cob ground  
13      woody ring portion; corn cob chaff portion; cotton seed  
14      stems; flax stems; wheat stems; sunflower seed stems;  
15      soybean stems; maize stems; rye grass stems; millet  
16      stems; and mixtures thereof.

1       7. The additive of claim 2 wherein the polymer is a  
2       partially hydrolyzed polyacrylamide.

1       8. The additive of claim 7 wherein the reinforcing  
2       material is a comminuted material selected from among  
3       comminuted materials derived from peanuts, wood, paper  
4       any portion of rice seed or plant, any portion of corn  
5       cobs, and mixtures thereof.

1       9. The additive of claim 8 wherein the additive further  
2       includes cellophane, and wherein the reinforcing material  
3       is a comminuted material selected from among mixtures of  
4       comminuted rice fraction and peanut hulls; mixtures of  
5       comminuted rice fraction, and wood fiber or almond hulls;  
6       mixtures of comminuted rice fraction and corn cob  
7       fraction; and mixtures of comminuted rice fraction and  
8       corn cob fraction and at least one of wood fiber, nut  
9       shells, and paper.

1       10. The additive of claim 9 wherein the reinforcing  
2       material comprises comminuted mixture of rice fraction,  
3       corn cob pith and chaff, cedar fiber, nut shells, and  
4       paper.

1       11. A method of forming a tubing/casing annulus plug  
2       fluid comprising:

3                   (a) providing a tubing/casing annulus plug additive  
4                   comprising a dry mixture of water soluble crosslinkable  
5                   polymer, a crosslinking agent, and a reinforcing material  
6                   selected from among fibers and comminuted plant  
7                   materials; and

8                   (b) contacting the tubing/casing annulus plug  
9                   additive with water or an aqueous solution to form the  
10                  tubing/casing annulus plug fluid.

1                   12. The method of claim 11 wherein the polymer is a  
2                   partially hydrolyzed polyacrylamide, the crosslinking  
3                   agent is a chromic carboxylate complex, wherein the  
4                   additive further includes cellophane, and wherein the  
5                   reinforcing material is a comminuted material selected  
6                   from among mixtures of comminuted rice fraction and  
7                   peanut hulls; mixtures of comminuted rice fraction, and  
8                   wood fiber or almond hulls; mixtures of comminuted rice  
9                   fraction and corn cob fraction; and mixtures of  
10                  comminuted rice fraction and corn cob fraction and at  
11                  least one of wood fiber, nut shells, and paper.

1                   13. The additive of claim 12 wherein the reinforcing  
2                   material comprises comminuted mixture of rice fraction,

3 corn cob pith and chaff, cedar fiber, nut shells, and  
4 paper.

1 14. A method for plugging a tubing/casing annulus formed  
2 between a casing and a tube internal to the casing in a  
3 wellbore in fluid communication with a subterranean  
4 hydrocarbon-bearing formation, the method comprising:

5 (a) providing a tubing/casing annulus plug additive  
6 comprising a dry mixture of water soluble crosslinkable  
7 polymer, a crosslinking agent, and a reinforcing material  
8 selected from among fibers and comminuted plant  
9 materials;

10 (b) contacting the tubing/casing annulus plug  
11 additive with water or an aqueous solution to form a  
12 tubing/casing annulus plug fluid;

13 (c) injecting the tubing/casing annulus plug fluid  
14 into the annulus; and

15 (d) crosslinking said fluid to substantial  
16 completion in said annulus to substantially plug said  
17 annulus.

1 15. The method of claim 14 wherein the polymer is an a  
2 carboxylate-containing polymer and the crosslinking agent  
3 is a chromic carboxylate complex.

1 16. The method of claim 15 wherein the reinforcing  
2 material comprises hydrophilic and hydrophobic fibers.

1 17. The method of claim 16 wherein the hydrophobic  
2 fibers comprise at least one selected from the group of  
3 hydrophobic fibers consisting essentially of nylon,  
4 rayon, and hydrocarbon fibers, and wherein the  
5 hydrophilic fibers comprise at least one selected from  
6 the group of hydrophilic fibers consisting essentially of  
7 glass, cellulose, carbon, silicon, graphite, calcined  
8 petroleum coke, and cotton fibers.

1 18. The method of claim 15 wherein the reinforcing  
2 material comprises comminuted plant material.

1 19. The method of claim 18 wherein the reinforcing  
2 material comprises at least one comminuted material  
3 selected from the group of comminuted plant materials  
4 consisting essentially of nut and seed shells or hulls of  
5 almond, brazil, cocoa bean, coconut, cotton, flax, grass,  
6 linseed, maize, millet, oat, peach, peanut, rice, rye,  
7 soybean, sunflower, walnut, and wheat; rice tips; rice  
8 straw; rice bran; crude pectate pulp; peat moss fibers;

9 flax; cotton; cotton linters; wool; sugar cane; paper;  
10 bagasse; bamboo; corn stalks; sawdust; wood; bark; straw;  
11 cork; dehydrated vegetable matter; whole ground corn  
12 cobs; corn cob light density pith core; corn cob ground  
13 woody ring portion; corn cob chaff portion; cotton seed  
14 stems; flax stems; wheat stems; sunflower seed stems;  
15 soybean stems; maize stems; rye grass stems; millet  
16 stems; and mixtures thereof.

1 20. The method of claim 15 wherein the polymer is a  
2 partially hydrolyzed polyacrylamide.

1       21. The method of claim 20 wherein the reinforcing  
2       material is a comminuted material selected from among  
3       comminuted materials derived from peanuts, wood, paper  
4       any portion of rice seed or plant, any portion of corn  
5       cobs, and mixtures thereof.

1 22. The method of claim 21 wherein the additive further  
2 includes cellophane, and wherein the reinforcing material  
3 is a comminuted material selected from among mixtures of  
4 comminuted rice fraction and peanut hulls; mixtures of  
5 comminuted rice fraction, and wood fiber or almond hulls;  
6 mixtures of comminuted rice fraction and corn cob

7 fraction; and mixtures of comminuted rice fraction and  
8 corn cob fraction and at least one of wood fiber, nut  
9 shells, and paper.

1 23. The method of claim 22 wherein the reinforcing  
2 material comprises comminuted mixture of rice fraction,  
3 corn cob pith and chaff, cedar fiber, nut shells, and  
4 paper.

1 24. A method for plugging a tubing/casing annulus formed  
2 between a casing and a tube internal to the casing in a  
3 wellbore in fluid communication with a subterranean  
4 hydrocarbon-bearing formation, the method comprising:

5 (a) providing a tubing/casing annulus plug additive  
6 comprising an aqueous solution of water soluble  
7 crosslinkable polymer, a crosslinking agent, and a  
8 reinforcing material selected from among fibers and  
9 comminuted plant materials;

10 (b) injecting the tubing/casing annulus plug fluid  
11 into the annulus; and

12 (c) crosslinking said fluid to substantial  
13 completion in said annulus to substantially plug said  
14 annulus.

1 25. The method of claim 24 wherein the polymer is an a  
2 carboxylate-containing polymer and the crosslinking agent  
3 is a chromic carboxylate complex.

1 26. The method of claim 25 wherein the reinforcing  
2 material comprises hydrophilic and hydrophobic fibers.

1 27. The method of claim 26 wherein the hydrophobic  
2 fibers comprise at least one selected from the group of  
3 hydrophobic fibers consisting essentially of nylon,  
4 rayon, and hydrocarbon fibers, and wherein the  
5 hydrophilic fibers comprise at least one selected from  
6 the group of hydrophilic fibers consisting essentially of  
7 glass, cellulose, carbon, silicon, graphite, calcined  
8 petroleum coke, and cotton fibers.

1 28. The method of claim 25 wherein the reinforcing  
2 material comprises comminuted plant material.

1 29. The method of claim 28 wherein the reinforcing  
2 material comprises at least one comminuted material  
3 selected from the group of comminuted plant materials  
4 consisting essentially of nut and seed shells or hulls of  
5 almond, brazil, cocoa bean, coconut, cotton, flax, grass,

6 linseed, maize, millet, oat, peach, peanut, rice, rye,  
7 soybean, sunflower, walnut, and wheat; rice tips; rice  
8 straw; rice bran; crude pectate pulp; peat moss fibers;  
9 flax; cotton; cotton linters; wool; sugar cane; paper;  
10 bagasse; bamboo; corn stalks; sawdust; wood; bark; straw;  
11 cork; dehydrated vegetable matter; whole ground corn  
12 cobs; corn cob light density pith core; corn cob ground  
13 woody ring portion; corn cob chaff portion; cotton seed  
14 stems; flax stems; wheat stems; sunflower seed stems;  
15 soybean stems; maize stems; rye grass stems; millet  
16 stems; and mixtures thereof.

1 30. The method of claim 25 wherein the polymer is a  
2 partially hydrolyzed polyacrylamide.

1 31. The method of claim 30 wherein the reinforcing  
2 material is a comminuted material selected from among  
3 comminuted materials derived from peanuts, wood, paper  
4 any portion of rice seed or plant, any portion of corn  
5 cobs, and mixtures thereof.

1 32. The method of claim 31 wherein the additive further  
2 includes cellophane, and wherein the reinforcing material  
3 is a comminuted material selected from among mixtures of

4. comminuted rice fraction and peanut hulls; mixtures of  
5. comminuted rice fraction, and wood fiber or almond hulls;  
6. mixtures of comminuted rice fraction and corn cob  
7. fraction; and mixtures of comminuted rice fraction and  
8. corn cob fraction and at least one of wood fiber, nut  
9. shells, and paper.

1. 33. The method of claim 32 wherein the reinforcing  
2. material comprises comminuted mixture of rice fraction,  
3. corn cob pith and chaff, cedar fiber, nut shells, and  
4. paper.